

(12) UK Patent Application (19) GB (11) 2 113 457 A

(21) Application No 8235610

(22) Date of filing 14 Dec 1982

(30) Priority data

(31) 330128

(32) 14 Dec 1981

(33) United States of America  
(US)

(43) Application published  
3 Aug 1983

(51) INT CL<sup>3</sup>  
H01M 10/36

(52) Domestic classification  
H1B 1036 440 458

(56) Documents cited  
None

(58) Field of search  
H1B

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(54) Inorganic rechargeable  
non-aqueous cell

(57) A totally inorganic non-aqueous rechargeable cell having an alkali or alkaline earth metal anode such as of lithium, a sulphur dioxide-containing electrolyte and a discharging metal halide cathode, such as of  $\text{CuCl}_2$ , with said metal halide being substantially totally insoluble in  $\text{SO}_2$ .

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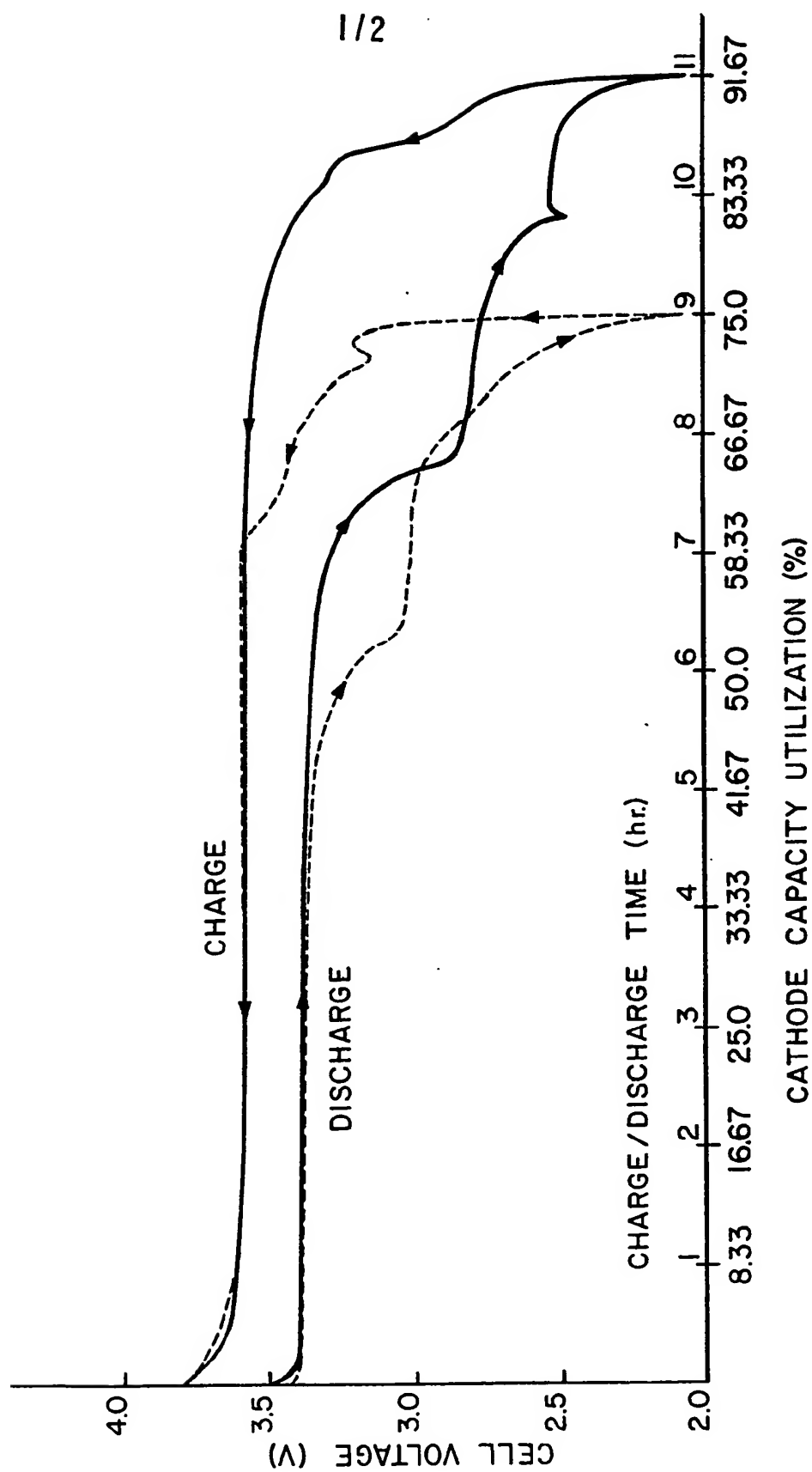


Fig. 1

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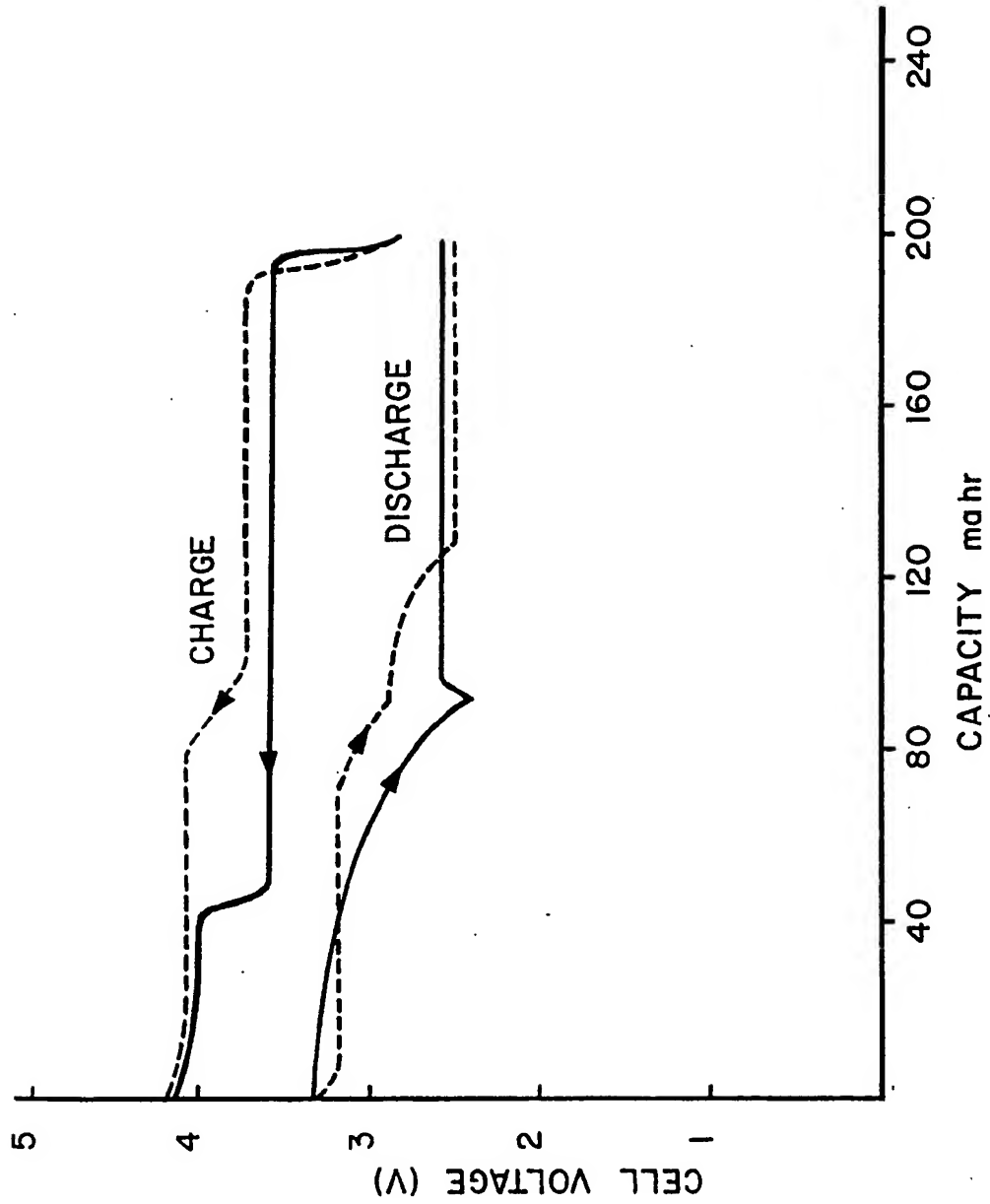


Fig. 2

## SPECIFICATION

## Inorganic rechargeable non-aqueous cell

5 This invention relates to non-aqueous rechargeable cells and more particularly to such cells having lithium anodes and sulfur dioxide electrolyte solvents.

The rechargeability of non-aqueous cells has been  
10 generally hampered by the presence within such cells of materials which react either upon standing or during cell discharge and which are not capable of being completely regenerated from their reaction products during cell charging. Organic electrolyte  
15 solvents utilized in non-aqueous cells such as propylene carbonate which forms anode metal carbonates and propylene gas are the most common of the incompletely regenerable materials. However, such organic electrolyte solvents are generally indispensable for proper operation of the non-aqueous cells  
20 particularly cells having sulfur dioxide electrolyte solvent/cathode depolarizers, since sulfur dioxide alone is a poor solvent for electrolyte salts except for certain esoteric salts such as clovoborates and  
25 gallium halides as described in U.S. Patents Nos. 4,020,240 and 4,177,329 respectively. More common salts such as metal halides; e.g., LiBr and tetrachloroaluminates e.g.,  $\text{LiAlCl}_4$  are either insoluble in  $\text{SO}_2$  alone or form complexes therewith whereby cell  
30 performance is drastically deteriorated. Utilization of the aforementioned esoteric salts in order to provide a totally inorganic cell has been effective in increasing the rechargeable efficiency of such cells. However, some of the esoteric salts, while effective, are  
35 nevertheless exceedingly costly whereby construction of an economical cell therewith has been generally precluded. Furthermore, during the increased cycle life in such cells a second source of deterioration of the cells was discovered. In cells  
40 containing the inorganic sulfur dioxide electrolyte and inert carbon cathodes said cathodes tended to lose their structural integrity. The formation and depletion of cell reaction products within the cathode causes detrimental expansion and contraction of the carbon cathode which expansion and  
45 contraction could not be accommodated without structural damage to the cathode.

It is an object of the present invention to provide an improved totally inorganic non-aqueous cell  
50 which is readily and efficiently rechargeable.

It is a further object of the present invention to provide such cell with readily obtainable and economical components.

These and other objects, features and advantages  
55 of the present invention will be more readily apparent from the following discussion and the drawings in which:

*Figure 1* is a discharge-charge graph of cells made in accordance with the present invention and

60 *Figure 2* is a discharge-charge graph of another embodiment of a cell made in accordance with the present invention.

Generally, the present invention comprises an efficiently rechargeable totally inorganic non-  
65 aqueous cell containing an anode of an alkali or

alkaline earth metal preferably lithium, including alloys and mixtures, a totally inorganic electrolyte comprised of sulfur dioxide with an electrolyte salt soluble therein dissolved therein, and an insoluble  
70 (in said sulfur dioxide) metal halide cathode which discharges during cell operation in preference to the  $\text{SO}_2$ . Metal salts such as  $\text{FeCl}_3$  which are soluble in  $\text{SO}_2$  are accordingly generally not within the purview of the present invention. In order to prevent such  
75  $\text{SO}_2$  discharge and for greater cell capacity it is preferred that the metal halide provides a potential greater than that obtainable from the  $\text{SO}_2$  as a cathode depolarizer. However, even with metal halides of lower potential the  $\text{SO}_2$  electrolyte solvent  
80 is substantially prevented from being discharged in preference to the metal halide because the insoluble metal halide cathode does not provide a catalytic surface for the discharge of the  $\text{SO}_2$  as compared to inert carbon cathodes.

In a preferred embodiment of the present invention the cell is comprised of a lithium anode and a copper chloride ( $\text{CuCl}_2$ ) cathode. It has been discovered that the previously unsuitable but economical salts such as  $\text{LiAlCl}_4$  (which while soluble in the  $\text{SO}_2$   
90 detrimentally complexed therewith) could be effectively utilized in the cells of the present invention. This utility is believed to be attributable to the fact that  $\text{SO}_2$  in the cell is not discharged and that its complexing with the salt does not as a result affect  
95 cell capacity or performance. It is therefore preferred from an economic standpoint, to utilize tetrachloroaluminate salts such as  $\text{LiAlCl}_4$  as the electrolyte salt. This does not however preclude the utilization of other salts such as  $\text{LiGaCl}_4$ ,  $\text{Li}_2\text{B}_{10}\text{Cl}_{10}$  and the like  
100 as electrolyte salts provided that they are soluble in the  $\text{SO}_2$  without the necessity for organic cosolvents. Preferably such salts are anode metal salts.

Though metal halides such as copper chloride have been utilized as cathodes in non-aqueous cells,  
105 such cells have invariably contained organic solvents in which the halides such as copper chloride were at least partially soluble. As a result such cells were considered to be unsatisfactory because of the inherent problem of self discharge caused by the solvated metal halide. However, the very deficiency  
110 of  $\text{SO}_2$ , that it is a poor solvent without organic cosolvents, renders the present invention operable since the metal halides such as copper chloride are substantially totally insoluble in  $\text{SO}_2$  alone.

The metal halide cathode is preferably made from a compressed mixture of the metal halide, conductive materials such as graphite or carbon and a binder such as polytetrafluoroethylene. The preferred percentage of the metal halide is between 60%  
120 and 80% by weight with the remainder being the conductive material (about 30 to 10%) and binder (about 10%). The higher the intended rate the greater the amount of conductive materials.

In order to more clearly illustrated the efficacy of the present invention, the following examples are  
125 presented. It is understood that such examples are for illustrative purposes only and that specifics contained therein are not to be construed as limitations on the present invention. Unless otherwise  
130 indicated all parts and percentages are by weight.

*Example 1*

Flat cells were made with each having two anode layers of lithium foil ( $1 \times 1.6 \times 0.020''$  or  $2.54 \times 4.06 \times 0.05$  cm) pressed onto a copper foil ( $0.020''$  or  $0.05$  cm), about 25 grams of  $0.5 M$   $\text{LiGaCl}_4\text{-SO}_2$  electrolyte, and four grams of a compressed (20,000 psi or  $1406 \text{ Kg/cm}^2$ ) mixture of 60%  $\text{CuCl}_2$ , 30% graphite and 10% polytetrafluoroethylene (PTFE) on an expanded nickel grid as the cathode ( $1 \times 1.6 \times 0.065''$  or  $2.54 \times 2.54 \times 4.06 \times 0.16$  cm). The anode layers and cathode were individually heat sealed inside sheets of microporous polypropylene and the anode layers placed one on each side of the cathode. Two cells were each discharged at a rate of  $2 \text{ mA/cm}^2$  or  $40 \text{ mA}$  and thereafter charged in a cycling regimen with a 2 volt cutoff for charging. The theoretical capacity of the cells was 480mAh (limiting cathode capacity. Anode capacity was about 1800 mAh.). Figure 1 depicts the cycling efficiency of the cells with one cell shown by the solid line after the 4th cycle and the broken line indicating the second cell after the 70th cycle (a short circuit in the first cell prematurely ended its cycling life after about 60 cycles). The second cell was cycled 101 times but with diminished capacity and delivered about 67 times the  $\text{CuCl}_2$  capacity on voltage cycling and 18 anode turnovers. The average voltage is relatively high at about 3.3 volts as compared to the discharge voltage of  $\text{SO}_2$  of about 2.9 volts.

*Example 2*

A cell was made as in Example 1 but with a  $1 M$   $\text{LiAlCl}_4\text{-SO}_2$  electrolyte and a 2 gram cathode. The cell was discharged at the same rate of  $2 \text{ ma/cm}^2$  and charged at  $1 \text{ ma/cm}^2$  with discharge-charge cycling being on a timed basis of 4.9 hr. discharge and 9.8 hr. charge. The cell underwent 23 cycles and Figure 2 depicts the curves for the first cycle (solid line) and twenty-first cycle (broken line) with the cell actually improving over continued cycling.

## CLAIMS

1. A totally inorganic rechargeable non-aqueous electrochemical cell comprising an anode of alkali or alkaline earth metal, an electrolyte comprised of an electrolyte salt dissolved in sulphur dioxide, said electrolyte being free of organic solvents, and a cathode comprised of a cathode-active metal halide insoluble in said sulphur dioxide.

2. The cell of claim 1 wherein said metal halide provides a potential greater than that provided by the sulphur dioxide.

3. The cell of claim 2 wherein said metal halide is  $\text{CuCl}_2$ .

4. The cell of claim 1, 2 or 3 wherein said anode is comprised of lithium.

5. The cell of claim 1, 2, 3 or 4 wherein said electrolyte salt is a gallium halide salt.

6. The cell of claim 1, 2, 3 or 4, wherein said electrolyte salt is an aluminium halide salt.

7. The cell of claim 1, in which the anode metal is lithium, the electrolyte consists essentially of  $\text{LiAlCl}_4$  dissolved in  $\text{SO}_2$ , and the cathode comprises  $\text{CuCl}_2$ .

8. The cell of claim 1 in which the anode metal is

lithium, the electrolyte consists essentially of  $\text{LiGaCl}_4$  dissolved in  $\text{SO}_2$ , and the cathode comprises  $\text{CuCl}_2$ .

9. A cell substantially as set forth in the foregoing Example 1 or Example 2.

Printed for Her Majesty's Stationery Office, by Croydon Printing Company Limited, Croydon, Surrey, 1983.  
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

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